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Portable Amperometric Perchlorate Selective Sensors with Microhole Array-water/organic Gel Interfaces

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A novel stick-shaped portable sensing device featuring a microhole array interface between the polyvinyl-chloride-2-nitrophenyloctylether (PVC-NPOE) gel and water phase was developed for *in-situ* sensing of perchlorate ions in real water samples. Perchlorate sensitive sensing responses were obtained based on measuring the current changes with respect to the assisted transfer reaction of perchlorate ions by a perchlorate selective ligand namely, bis(dibenzoylmethanato)Ni(II) ($Ni(DBM)_2$) across the polarized microhole array interface. Cyclic voltammetry was used to characterize the assisted transfer reaction of perchlorate ions by the $Ni(DBM)_2$ ligand when using the portable sensing device. The current response for the transfer of perchlorate anions by $Ni(DBM)_2$ across the micro-water/gel interface linearly increased as a function of the perchlorate ion concentration. The technique of differential pulse stripping voltammetry was also utilized to improve the sensitivity of the perchlorate anion detection down to 10 ppb. This was acquired by preconcentrating perchlorate anions in the gel layer by means of holding the ion transfer potential at 0 mV (*vs*. Ag/AgCl) for 30 s followed by stripping the complexed perchlorate ion with the ligand. The effect of various potential interfering anions on the perchlorate sensor was also investigated and showed an excellent selectivity over Br^-, NO_2^-, NO_3^-, CO_3^{2-}, CH_3COO^- and SO_4^{2-} ions. As a final demonstration, some regional water samples from the Sincheon river in Daegu city were analyzed and the data was verified with that of ion chromatography (IC) analysis from one of the Korean-certified water quality evaluation centers.

Key Words : Perchlorate selective sensor, Portable sensor, Microhole array-water/gel interface, Ion transfer reaction, Bis(dibenzoylmethanato)Ni(II)

Introduction

Perchlorate is regarded as an environmentally toxic reagent known to affect hormone regulation and the onset of various diseases including cancer and neurological problems.[1,2] In July 2006, an industrial accident in the Nakdong river region (South Korea) resulted in a perchlorate concentration of 2.23 ppm, which is about 150 times higher than that of the US Environmental Protection Agency (EPA) permitted level (15 ppb). Following this, the S. Korean Ministry of Environment and National Institute of Environmental Research (NIER) has established strong regulations on acceptable levels of perchlorate in drinking water, setting it at 15 ppb in 2010.[3] Therefore, there have been greater demands for the development of techniques for the fast and real time detection of perchlorate ions at a ppb levels in environmental water samples.

Conventional methods for analyzing perchlorate anions in aqueous samples are ion chromatography-mass spectrometry (IC-MS),[4] IC,[5] liquid chromatography-MS/MS,[6] and Raman spectroscopy[7] which have each been demonstrated to show excellent accuracy and precision in determining the perchlorate anion concentration down to 0.015 ppb, 0.43 ppb, 0.020-2.36 μg/kg, and 10-100 ppb levels, respectively. However, it usually requires well trained technicians to operate such instruments in addition to collecting and transporting representative samples for accurate and precise analysis in the laboratory. A field applicable sensing device with fast and sensitive detection capability can be an excellent alternative. Some recent examples on the development of disposable or portable sensing platforms include optical and electrochemical methods for field applications.[8-13] In particular, electrochemical sensors are excellent candidates for portable sensors since they can be easily miniaturized and can also possess real-time measurement capability and are sensitive enough to analyze ppb levels.[8,11] For example, Gertsch *et al.*[8] reported a microchip capillary electrophoresis (MCE) device using a conductivity detection method for the selective detection of perchlorate anions with a detection limit of 3.4 ± 1.8 ppb in standard water samples. Ion transfer reaction at the interface between two immiscible electrolyte solutions (ITIES) is an alternative which has been used as a platform for selective ion amperometric sensing.[14] Also, there have been extensive research works on developing detection platforms based on measuring currents associated with the charge transfer across a wide range of different

ITIES.[14-18] In particular, the use of a microhole array interface between water and polymerized organic gel layers has been successfully applied as a sensitive detection platform for heavy metal ions,[19] neurotoxins *via* an enzymatic reaction[20] alongside recent examples for anions and proteins.[21-24]

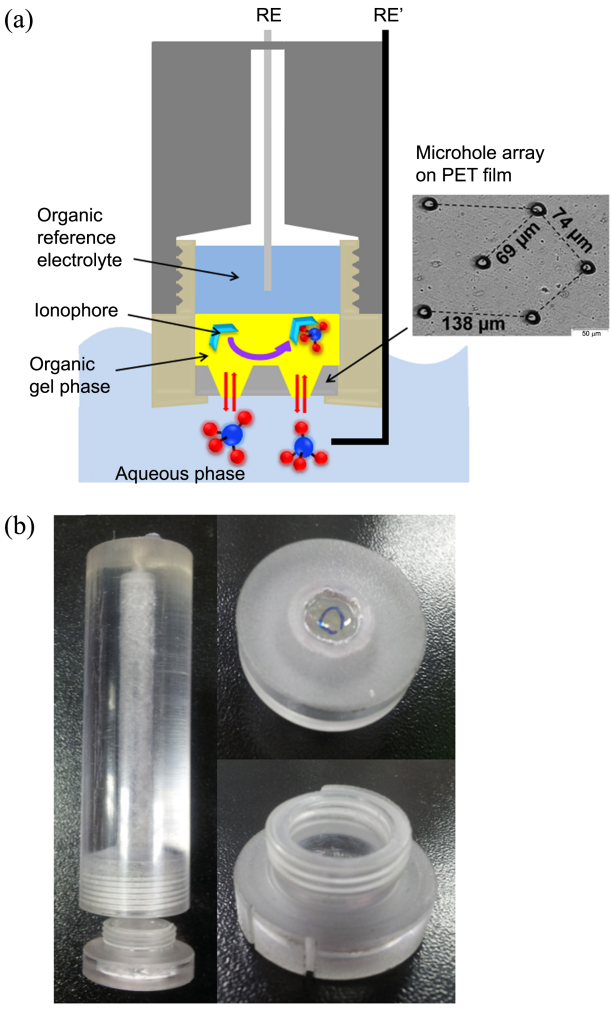
In this paper, we describe a portable real-time amperometric sensor for the selective and sensitive detection of perchlorate anions based on measuring the current response related to the assisted transfer of ClO_4^- ions by bis(dibenzoylmethanato)Ni(II) ($Ni(DBM)_2$) across the microhole array interface between the water/PVC-NPOE gel layer. *In-situ* portable sensing devices composed of the micro-water/gel interface were first designed and their electrochemical responses were characterized using cyclic voltammetry and differential pulse stripping voltammetry. As a further demonstration, we applied the developed sensor for the selective sensing of perchlorate anions in regional river samples alongside the optimization of interference anion effects.

Experimental

Reagents. Sodium perchlorate ($NaClO_4$, Sigma-Aldrich), nickel(II)acetate tetrahydrate (Sigma-Aldrich), 1,3-diphenyl-1,3-propanedione (Sigma-Aldrich), ethanol (OCI), 2-nitrophenyloctylether (NPOE, Fluka), polyvinylchloride (PVC, high molecular weight, Sigma-Aldrich), sodium chloride (NaCl, Merck), lithium chloride (LiCl, Fluka), tetramethylammonium chloride (TMACl, > 97%, Sigma-Aldrich), sodium bromide (NaBr, Sigma-Aldrich), sodium thiocyanate (NaSCN, Sigma-Aldrich), sodium cyanide (NaCN, Sigma-Aldrich), sodium nitrite ($NaNO_2$, Sigma-Aldrich), sodium acetate ($NaCH_3COO$, Sigma-Aldrich), sodium carbonate (Na_2CO_3, Sigma-Aldrich), sodium sulfate (Na_2SO_4, Sigma-Aldrich), sodium iodide (NaI, Sigma-Aldrich), sodium nitrate ($NaNO_3$, Sigma-Aldrich), tetraoctylammonium bromide (TOABr, Fluka), lithium tetrakis(pentafluorophenyl)borate etherate (LiTB, Boulder Scientific Co.) and tetraoctylammonium chloride (TOACl, Sigma-Aldrich) were all used as received. Perchlorate standard solution of IC was purchased from Accustandard. The supporting electrolyte for the organic phase, tetraoctylammonium tetrakis(pentafluorophenyl)borate (TOATB) was prepared using previously reported method.[21] All aqueous solutions were prepared using Millipore-filtered water.

Synthesis of Bis(dibenzoylmethanato)Ni(II) [$Ni(DBM)_2$] Complex. Bis(dibenzoylmethanato)Ni(II) [$Ni(DBM)_2$] complex was synthesized following the method reported by Ripmeester *et al.*[25] Briefly, a 10 mM Nickel(II) acetate tetrahydrate and 10 mM 1,3-diphenyl-1,3-propanedione was dissolved in a 150 mL solution of 90% ethanol and 10% water and stirred for 1 hour at 150 °C. The solution was then cooled down at room temperature. Next, the complex was refluxed at 130 °C in oil bath for 2 hours while stirring. The product was then filtered and washed several times using 90% ethanol followed by drying under vacuum. $Ni(DBM)_2$ complex was kept in dry oven.

Stick-shape Portable Sensors. For real-time measurements of ClO_4^- ions, we designed a novel stick shape portable sensing platform which can accommodate the water/gel interface. Scheme 1 shows a schematic of a stick-shape portable sensor alongside a photograph showing each compartment. The sensor is divided into two parts: (i) the head part composed of a PET membrane featuring a microhole array filled with the PVC-NPOE gel and the protruding part of the head filled with the organic supporting electrolyte, and (ii) the main body part has a narrow empty hole where a long Ag/AgCl wire reference electrode for the organic phase can be inserted enabling contact with the supporting electrolyte. A long groove made on the outer surface of the main body is to fit the reference electrode for the aqueous phase which is long enough to be in contact with any water samples. Finally the head part was screwed to fit into the main body. Both Ag/AgCl wire electrodes were used longer than that of the main body in order to be connected to a portable potentiostat.



Scheme 1. (a) Schematics showing the stick-type portable sensing device incorporating the microhole array-water/PVC-NPOE gel interface for the selective sensing of perchlorate anions. A representative microscopy image featuring microholes in a 66 microhole array is also shown. (b) Photographs of the *in-situ* portable sensing device.

Fabrication of Microhole Array-liquid/gel Interface. A

66 (11 × 6) microhole array was created by drilling a polyethylene terephthalate film (PET, 12 μm thick, Melinex type 'S' from ICI Films, UK) using a UV Excimer laser.[26] The diameter of each microhole was determined as around 14 μm and 9.6 μm for the entrance and exit side, respectively (See Scheme 1(a)). Twelve microliters of the organic gel solution containing PVC (2.8% w/w) and 10 mM TOATB dissolved in NPOE were casted at 80 °C on the exit side of the 66 microhole array of PET film and kept for minimum 6 h to be gelified. The average radius of each microhole array-water/PVC-NPOE gel interface is about 4.8 μm while the average centre to centre distance between two neighboring microholes in the 66 microhole array (approximately 94 μm) is at least 10 times larger than that of each microhole radii. This is to avoid any overlap of diffusion zones between the inter-microholes and ensures each microholes act as an individual water/gel interface.[26]

Electrochemical Measurements. All electrochemical experiments were performed using two different potentiostats, a stand-alone Autolab PGSTAT30 (Ecochemie) and a portable Vertex (IVIUM technology), in a two electrode mode without any IR drop compensation. All experiments were carried out at room temperature.

Results and Discussion

Electrochemical Characterization of Assisted Transfer Reaction of Perchlorate Anions by $Ni(DBM)_2$ Across a Micro-liquid/gel Interface Assembled in a Stick-type Portable Device. A novel field applicable portable sensing device incorporating a microhole array interface between the water and organic gel phase is designed as shown in Scheme 1 alongside the details in the Experimental section. Prior to any field-based measurements, the portable sensor was characterized in terms of measuring the current changes with respect to the assisted transfer reaction of perchlorate anions by $Ni(DBM)_2$ across the micro-water/gel interface. The transfer reaction of perchlorate anions across the microhole array-liquid/gel interface were studied using the electrochemical cell setup described in Cell 1.

A series of cyclic voltammograms were first obtained for various concentrations of perchlorate anion transferring from the water to organic phase and also transferring back from the organic to water phase across a polarized liquid/PVC-NPOE gel interface. The concentration of NaCl was fixed at 10 mM. In the absence of perchlorate (Figure 1), no steady-state current was observed within the available potential window. When perchlorate anions were added into the aqueous phase, a steady-state current on the forward scan at −7.5 mV (*vs*. Ag/AgCl) was acquired mainly due to the hemi-spherical diffusion of perchlorate ions transferring

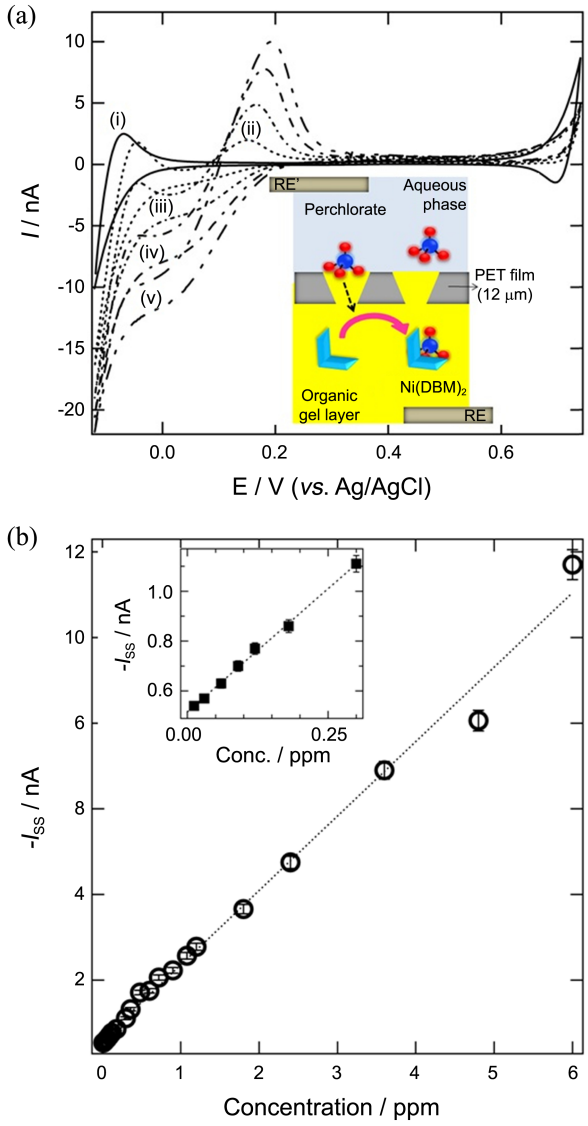
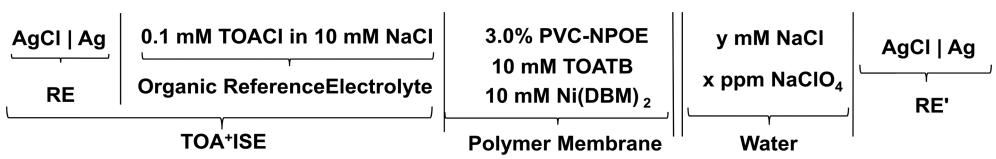


Figure 1. (a) Representative cyclic voltammograms for the assisted transfer reaction of different concentrations of perchlorate ions by $Ni(DBM)_2$ present in the PVC-NPOE gel layer using Cell 1. (i) 10 mM NaCl in the absence of ClO_4^- anions. Dotted lines are the CVs for the presence of (ii) 0.9 ppm, (iii) 2.4 ppm, (iv) 4.8 ppm and (v) 6 ppm perchlorate ions. Scan rate was 20 $mV \cdot s^{-1}$ and 0.1 mM TOACl was used as an organic supporting electrolyte. Inset shows a simplified schematic of the assisted transfer of perchlorate anions by $Ni(DBM)_2$ across the microhole array interface between the water and PVC-NPOE gel phases. (b) Plots of steady-state current responsible for perchlorate anion transfer versus the concentration of perchlorate anion. Perchlorate concentrations were 0.012, 0.03, 0.06, 0.09, 0.12, 0.18, 0.3, 0.36, 0.48, 0.6, 0.72, 0.9, 1.08, 1.2, 1.8, 2.4, 3.6, 4.8 up to 6 ppm. Inset is for the low concentration range of perchlorate ions from 0.012 ppm to 0.3 ppm. Some of data points were taken from Figure 1(a).



Cell 1

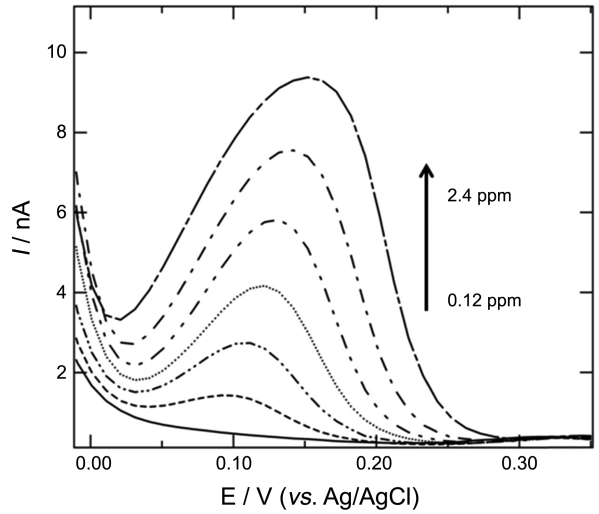


Figure 2. Representative differential pulse stripping voltammograms (DPSV) for the sensing of perchlorate anions at concentrations of 0.12, 0.3, 0.48, 0.72, 1.2 and 2.4 ppm (dotted lines). The solid line represents the DPSV obtained in the absence of perchlorate anions. The voltammogram was scanned from low to high potentials to strip the preconcentrated perchlorate ion from the organic gel layer to the aqueous phase. Holding for 30 s at a potential of 0 mV was performed to accumulate perchlorate anions in the gel layer. Potential increment = 10 mV, pulse duration = 50 ms and pulse potential = 50 mV.

from the aqueous to the organic phase across the microhole interface.[26] Whereas, a peak shaped voltammogram was obtained on the reverse scan due to the mixed diffusion regimes of linear and hemi-spherical flux from the perchlorate ion back from the viscous organic gel layer in the hole and outside the hole to the aqueous phase, respectively.[26]

Figure 1(b) shows a plot of the steady-state current changes as a function of perchlorate anions. The current increased linearly with respect to the perchlorate concentration ranging from 0.012 ppm to 6 ppm with a linear slope of 0.21 nA·ppm^{-1}. This is in good agreement with the theoretical slope of 0.16 nA·ppm^{-1} obtained using Eq. (1) for ion transfer reactions at an array of microhole-water/gel interfaces.[26]

$$I_{ss} = 4nmFD_{ClO_4^-}C_{ClO_4^-}r \quad (1)$$

where n is the charge number of ionic species, m is the number of microhole, F is the Faraday constant, $D_{ClO_4^-}$ is the diffusion coefficient of perchlorate ion as 1.27×10^{-5} cm^2·s^{-1},[27] $C_{ClO_4^-}$ is the concentration of perchlorate ion in water phase, and r (4.8 μm) is the radius of interface. A 120 ppb concentration of perchlorate anions could be detected within the signal to noise ratio of 3:1, which needs to be improved in order to be utilized for analyzing permeable levels of perchlorate in drinking water (below 15 ppb) from NIER.[3]

Differential pulse stripping voltammetry (DPSV) with a preconcentration step was thus applied to enhance the detection limit of the perchlorate anion portable sensor by holding the transferring potential of perchlorate ions from the aqueous to the organic gel phase at 0 mV (*vs.* Ag/AgCl) for 30s followed by the fast stripping of the ions back from the organic to the aqueous phase by means of scanning the potential from −0.12 V to 0.74 V with a potential step of 10 mV/s. Figure 2 shows DPS voltammograms for the different concentrations of perchlorate anions ranging from 120 ppb to 2.4 ppm. A peak current observed at around 0 mV corresponding to the stripping of the accumulated perchlorate anions from the gel layer to the aqueous phase increased proportionally as a function of the perchlorate ion concentration.

In order to demonstrate that the developed portable sensor can be applied to the real-time monitoring of river water samples that may not contain enough supporting electrolytes, DPSV response changes with respect to the perchlorate concentration were obtained for water samples both in the presence and the absence of any supporting electrolytes.

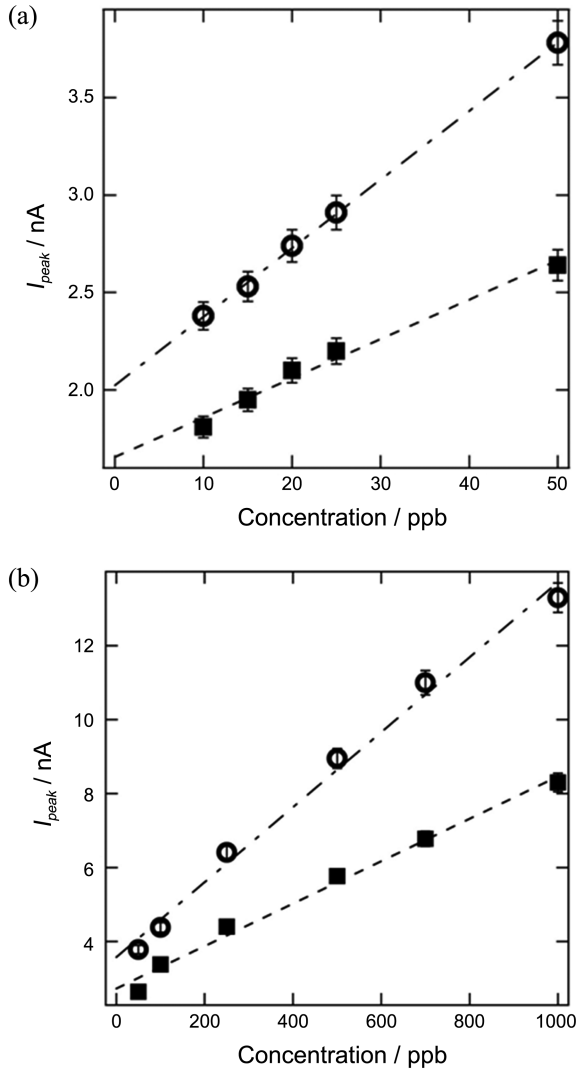


Figure 3. Plots of the peak current as a function of the perchlorate anion concentration from 10 ppb to 1 ppm for both the water sample in the presence and absence of supporting electrolytes. Perchlorate concentrations were varied (a) from 10 ppb to 50 ppb and (b) from 50 ppb to 1 ppm. The circles and squares represent data points from the analysis of perchlorate in the presence and absence of NaCl as an aqueous supporting electrolyte, respectively. Dotted line represents a linear fit to the data.

A series of plots showing the peak current versus the perchlorate concentration are presented in Figure 3. A perchlorate standard solution from Accustandard was used. One noticeable difference is the change in the slope for the calibration plots depending upon the water matrix; for the aqueous sample in the presence of 10 mM NaCl a linear fit with a slope of 0.03 nA·ppb^{-1} was obtained for the concentration range from 10 ppb to 50 ppb (see Fig. 3(a)). On the other hand, a slope of 0.02 nA·ppb^{-1} for the water in the absence of NaCl is obtained which is about 30% dampened than that when NaCl is added to the water phase. For the case of higher concentrations (50 ppb up to 1 ppm), a linear fit with a slope of 0.1 nA·ppb^{-1} and 0.05 nA·ppb^{-1} was obtained for the aqueous phase in the presence and absence of the supporting electrolyte, respectively (Fig. 3(b)). In both water sample cases, we can also conclude that our sensor is more sensitive when measuring a low ppm concentration range of perchlorate, which implicates that our sensor can be used for determining perchlorate in a low contamination level of environmental samples. A detectable concentration of 10 ppb perchlorate anions at a signal to noise ratio of 3:1 was achieved which is suitable for directly measuring the maximum allowed concentration of perchlorate in drinking water set as 15 ppb in S. Korea. Excellent reproducibility and chip to chip variation was obtained within an error of about 8% when tested over 50 sensor chips.

In order for further applicability to real sample analysis, the selectivity of the portable sensor for perchlorate anions in the presence of different anionic species including SCN^-, CN^-, I^-, NO_3^-, Br^-, NO_2^-, CO_3^{2-}, SO_4^{2-} and CH_3COO^- anions was investigated at a fixed concentration of 1.2 ppm perchlorate ions. Cell 2 was used.

In the hundred times excess presence of NO_3^-, Br^-, NO_2^-, CO_3^{2-}, SO_4^{2-}, CH_3COO^- anions, the perchlorate sensor did not show any responses. However, for the hundred times excess of SCN^-, CN^- and I^- anions, the perchlorate sensor responded significantly. This could still remain as a challenge for any ion selective sensing methodologies which can further improved by designing more selective ligand molecules for specific target ions. The selectivity coefficient ($\log k_{k,j}^{amp}$) for SCN^-, CN^- and I^- were estimated as −1.51, −2.15 and −1.55, respectively using the Eq. (2).

$$k_{k,j}^{amp} = (I_t - I_i)C_i / I_i C_j \quad (2)$$

where C is the concentration and i and j are the perchlorate and interfering anion, respectively, I_t is the total current responsible for both the perchlorate ion sensing current (I_i) and the interfering anion one.[28]

Portable Perchlorate Selective Sensors for Real Sample Analysis. As a final demonstration, the sensor was applied to the detection of perchlorate anions in samples taken from the Sincheon River in South Korea. The first sample was the water sample itself and the other two different samples were

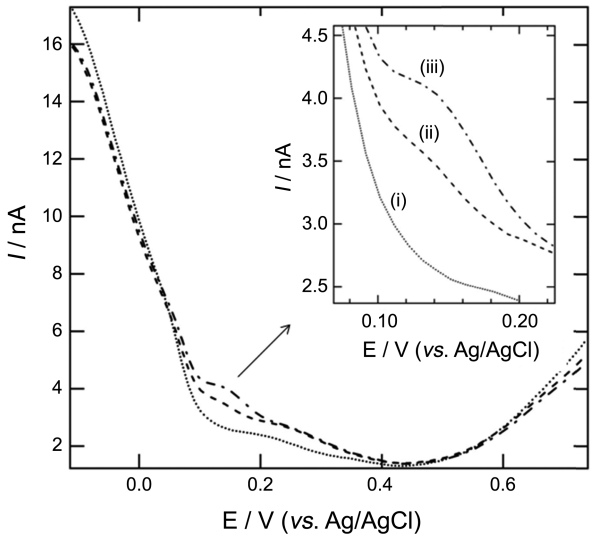
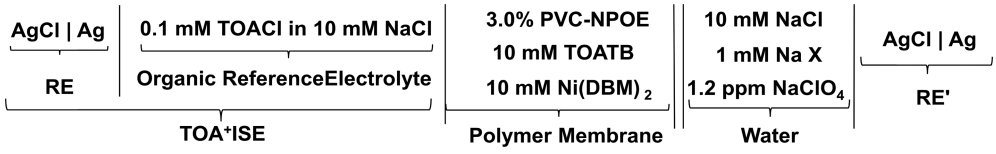


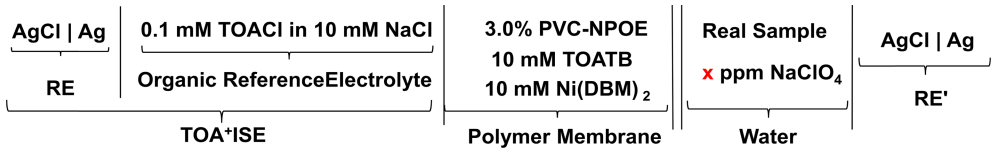
Figure 4. Differential pulse stripping voltammograms for Sincheon river water sample analysis. (i) Sincheon water sample. (ii) 50 ppb and (iii) 100 ppb of perchlorate standard solutions were added into the Sincheon sample (i). 0.1 mM TOACl was used as an organic supporting electrolyte. Holding for 30s at a potential of 0 mV was performed to accumulate perchlorate anions in the gel layer. Potential increment = 10 mV, pulse duration = 50 ms and pulse potential = 50 mV. Inset shows the close-up region where the peak current changes with respect to the addition of perchlorate anions.



Cell 2

Table 1. Comparison of real sample analyses utilizing the microhole array-water/NPOE sensor and IC method. Sample 1 is the sample from Shincheon river. Sample 2 and 3 are the Shincheon river water samples spiked with the perchlorate concentration of 50 and 100 ppb, respectively.

Sample number	Added perchlorate ion concentration (ppb)	Our sensor response (I_{peak}/nA)	Calibration plot in the presence of electrolyte (I_{peak}/nA)	Our method Verification (ppb)	IC Method (ppb)
1	0	–	–	–	–
2	50	3.57	3.78	**47**	55
3	100	4.03	4.38	**92**	106



Cell 3

prepared by adding different concentrations of perchlorate standard solutions to the river water. The DPSV analysis utilizing our sensor with Cell 3 is presented in Figure 4, which was compared to that obtained using a conventional IC method for the same samples.

Shincheon river water analysis data using our portable sensor were also compared to those of the standard IC analysis method summarized in Table 1. It was found that Shincheon water contained almost no perchlorate anions or below 10 ppb level of perchlorate as our sensor can detect the minimum of 10 ppb, also confirmed by the IC results in Table 1. As we added 50 and 100 ppb of the perchlorate standard solution into each of the Shincheon river water samples, the peak current responsible for perchlorate anions increased as a function of the added perchlorate concentration. The current increment with respect to the added standard perchlorate solution corresponded well with the calibration plot in the presence of NaCl electrolytes in Figure 3. An excellent agreement achieved in both the portable sensing and conventional IC method indicates that our method can be utilized for real-time analysis of perchlorate anions in any environmental water samples.

Conclusions

A novel *in-situ* amperometric sensing device integrating a microhole array-water/organic gel interface was developed for the sensitive detection of perchlorate anions down to 10 ppb. Ion transfer characteristics of the portable sensor featuring a microhole array-water/organic gel interface were identical to the conventional microhole interface electrochemical cell system. The portable sensor was successfully applied to determine the perchlorate anion concentration in environmental water samples and their results were in good agreement with the data from a conventional IC method. The developed portable sensors can also be applied to the detection of various environmentally toxic ionic species in real sample simply by tailoring different selective ionophores in the gel layer that can selectively interact with target ions.

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References

1. Urbansky, E. T. *Biorem. J.* **1998**, *2*, 81.
2. Greer, M. A.; Goodman, G.; Pleus, R. C.; Greer, S. E. *Environ. Health Perspect.* **2002**, *110*, 927.
3. http://water.nier.go.kr/waterBoard/waterBoardContent.do?seq=1229&boardType=weis/7_new s&frontYn=Y&returnUrl=/front/waterPress/waterNewsView.jsp
4. Kirk, A. B.; Dyke, J. V.; Ohira, S. I.; Dasgupta, P. K. *Sci. Total Environ.* **2013**, *443*, 939.
5. http://www.dionex.comen-uswebdocs4096-AN144-IC-Perchlorate-Fertilizer-Extracts AN7040 1_E.pdf
6. Lee, J. W.; Oh, S. H.; Oh, J. E. *J. Hazard. Mater.* **2012**, *243*, 52.
7. Gu, B.; Tio, J.; Wang, W.; Ku, Y. K.; Dai, S. *Appl. Spectrosc.* **2004**, *58*, 741.
8. http://serdp-estcp.org/Program-Areas/Environmental-Restoration/Contaminated-Groundwater/Monitoring/ER-1706/ER-1706/(modified)/14Jan2013
9. Li, X. A.; Zhou, D. M.; Xu, J. J.; Chen, H. Y. *Talanta* **2008**, *75*, 157.
10. Quang, L. X.; Lim, C. S.; Seong, G. H.; Choo, J. B.; Do, K. J.; Yoo, S. K. *Lab Chip*. **2008**, *8*, 2214.
11. Pumera, M. *J. Chromatogr. A* **2006**, *1113*, 5.
12. Tanyanyiwa, J.; Villar, E. M. A.; Abedul, M. T. F.; García, A. C.; Hoffmann, W.; Guber, A. E.; Herrmann, D.; Gerlach, A.; Gottschlich, N.; Hauser, P. C. *Analyst*. **2003**, *128*, 1019.
13. Wang, J.; Pumera, M.; Collins, G.; Opekar, F.; Jelínek, I. *Analyst.* **2002**, *127*, 719.
14. Samec, Z.; Samcová, E.; Girault, H. H. *Talanta* **2004**, *63*, 21.
15. Zazpe, R.; Hibert, C.; O'Brien, J.; Lanyon, Y. H.; Arrigan, D. W. M. *Lab Chip*. **2007**, *7*, 1732.
16. Rodgers, P. J.; Amemiya, S. *Anal. Chem.* **2007**, *79*, 9276.
17. Tong, Y.; Sun, P.; Zhang, Z.; Shao, Y. *J. Electroanal. Chem.* **2001**, *504*, 52.
18. Liu, B.; Shao, Y.; Mirkin, M. V. *Anal. Chem.* **2000**, *72*, 510.
19. Lee, H. J.; Lagger, G.; Pereira, C. M.; Silva, A. F.; Girault, H. H. *Talanta* **2009**, *78*, 66.
20. Hossain, M. M.; Faisal, S. N.; Kim, C. S.; Cha, H. J.; Nam, S. C.; Lee, H. J. *Electrochem. Commun*. **2011**, *13*, 611.
21. Hossain, M. M.; Girault, H. H.; Lee, H. J. *Bull. Korean Chem. Soc.* **2012**, *33*, 1734.
22. Hossain, M. M.; Lee, S. H.; Girault, H. H.; Devaud, V.; Lee, H. J. *Electrochim. Acta* **2012**, *82*, 12.
23. O'Mahony, A. M.; Scanlon, M. D.; Berduque, A.; Beni, V.; Arrigan, D. W. M.; Faggi, E.; Bencini, A. *Electrochem. Commun.* **2005**, *13*, 611.
24. Herzog, G.; Roger, A.; Sheehan, D.; Arrigan, D. W. M. *Anal. Chem.* **2010**, *82*, 258.
25. Soldatov, D. V.; Ripmeester, J. A. *Chem. Eur. J.* **2001**, *7*, 2979.
26. Lee, H. J.; Beattie, P. D.; Seddon, B. J.; Osborne, M. D.; Girault, H. H. *J. Electroanal. Chem.* **1997**, *440*, 73.
27. Peulon, S.; Guillou, V.; L'Her, M. *J. Electroanal. Chem.* **2001**, *514*, 94.
28. Maccà, C.; Wang, J. *Anal. Chim. Acta* **1995**, *303*, 265.